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STRUCTURAL CHANGES DURING MILLING OF ALUMINUM  
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16. Abstract  The mechanical activation of 4 fused corundum powders and a calcined Al <sub>2</sub> O <sub>3</sub> powder was studied. The milled powders were characterized by their structural properties, crystallite size, and lattice distortions, and powders. Structural changes during milling, detd. by x-ray line broadening anal., gave information about the enhanced activity of the powders caused by the lattice distortions and by the decreasing crystallite size during milling. The structural changes during milling, under the same milling conditions, can be quite different for the same ceramic material, but with different characteristics in the as-received state.			
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# STRUCTURAL CHANGES DURING MILLING OF ALUMINUM OXIDE POWDERS\*

G. Ziepler\*\*

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It is known that in the preparation and processing of ceramic powders a change in the characteristics of the powder can occur, e.g., in the size and distribution of the agglomerate and the particles and in the morphology of the powder particles, and also changes in the lattice structure of the particles can take place [1-15]. On the one hand, these changes can be regarded as occurrences accompanying these treatment processes, but on the other hand, it is known that they can serve to increase the mechanical activation of the powders, i.e., to increase their reactivity as a result of the increased energy content of the powders. Several questions then arise for the ceramicist who is interested in the preparation and processing of powders: Which treatment processes produce changes in the characteristics of the powders and how great are these changes? How can one achieve the highest possible mechanical activation of the raw powder for certain sinter products, e.g., by introducing a milling process? Which powder characteristics change during milling and how do different powders behave during the milling process?

This study is intended to make a contribution to these questions, in particular to the questions concerning the change in the properties of various ceramic powders during milling.

\* In a four-part series an X-ray measurement method (X-ray line-width analysis) for determining the characteristics of ceramic powders after different treatment processes is described. As an example, the structural changes during the milling and sintering of  $\text{Al}_2\text{O}_3$  powders are discussed. Part I: Keram. Z. 33(1981) 287-290.

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\*\*\* Numbers in margin indicate foreign pagination.

The mechanical activation of ceramic powders by means of milling.

The milling of powders is an important technological and industrial process and has thus been the object of many studies during milling [1-10,13,14]). Studies have been made of various oxides, also of  $Al_2O_3$  [2,3,8,13-15], of boehmite [6] and of hydrargillite [7]. During the milling process, which is very complex from the point of view of the material, morphological and lattice structure changes occur that have not yet actually been fully understood. In general, the surface area of the powders is increased during milling as a result of the reduction in size of the particles and the occurrence of fine cracks and roughening of the surfaces. With many materials two opposing effects are observed during milling: reduction in size of the large particles and agglomeration of small particles during further milling. Other changes can also take place during milling; changes in lattice construction, lattice conversion, partial amorphism of the crystalline solid and increased surface activity as a result of the unsaturated valences of fresh surface fractures. The changes in lattice construction during milling can be interpreted as changes in the order of the lattice which are caused by a decrease in crystallite size and by the occurrence of lattice distortions and lattice disturbances (by lattice disturbances is understood the shifting of the atoms from their ideal lattice positions → "the roughening of net planes"). With some materials longer milling can cure the lattice disturbances. The formation of new surfaces and the occurrence of lattice flaws during milling are connected with an energy increase in the powder. The morphological and lattice structure changes are dependent on the crystallographic construction of the material, on the type and manufacture of the powder, and on the type, intensity and duration of the energy produced.

Studies of oxides showed a reduction in particle size during milling - indicated by an increase in the surface area, a decrease in crystallite size and an increase in lattice distortions and lattice disturbances [2,3,8,9,13,14]. The decrease in crystallite size can be directly correlated to the increase in lattice disturbances. Further milling can produce an agglomeration of the

fine particles as the large particles are further reduced in size and before the milling equilibrium is reached. In the case of the aluminum oxide compounds, it should be mentioned further that the milling of boehmite and hydrargallite leads to a gradual amorphization [6, 7].

The mechanical activation of the powders indicated by the morphological and lattice structure changes leads to increased chemical reactivity and to improvement in the sinter properties. The increase in sinter activity as a result of milling can be explained by a rise in surface energy and an increase in the inner energy of the powder, i.e., the energy increase in the powder resulting from reduction of crystallite size and the occurrence of lattice distortions and disturbances. Studies of  $\text{Al}_2\text{O}_3$  have shown that during the milling of  $\text{Al}_2\text{O}_3$  powders the rise in inner energy can be considerably greater than the increase in surface energy [3].

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From this it can be concluded that in order to determine the powders activated by milling it is not sufficient to measure only the change in surface energy by measuring the surface area or size of the particles. It is far more important to determine the increase in sinter activity during milling through values that allow conclusions to be drawn about the increase in the inner energy on the powder. This is possible by measuring the structural changes, the change in crystallite size and lattice distortions, during individual milling periods. As was shown in Part I [16], the structural changes during milling can be measured by using linewidth analysis. The quantitative analysis of the measurements of an  $\text{Al}_2\text{O}_3$  powder shown in Figure 5 of Part I (lattice lines after various milling periods) is shown in Figure 1 in this part. The line of the curves clearly shows that mechanical activation during milling is indicated by a large increase in lattice distortions and a considerable decrease in crystallite size. As already explained above, the change in both of these values can be traced back to lattice flaws in the material and to fracturing processes in the particles during the milling process. The changes observed during milling enable conclusions to be drawn relating to the increase in inner energy of the powders.

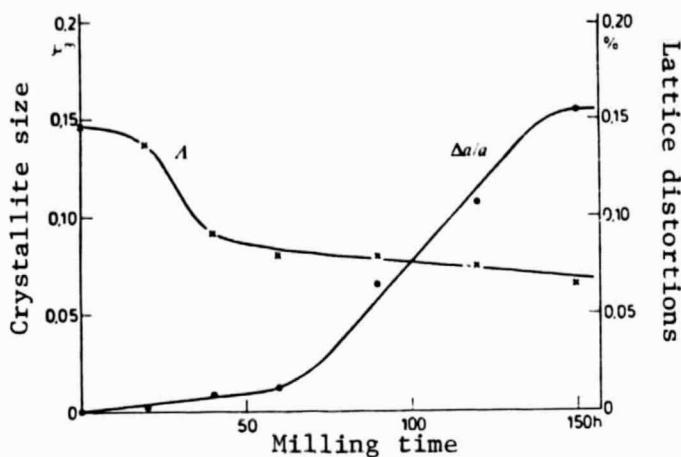


Figure 1. Structural changes during the milling of  $\text{Al}_2\text{O}_3$  powders, characterized by crystallite size and lattice distortions.

This contribution will discuss the change during milling in the characteristics of five different  $\text{Al}_2\text{O}_3$  powders (fused corundum and calcined powders) that can be used as raw materials for sinter products of high purity and density. The main thrust of this study is therefore the measurement of the changes in the structural properties of crystallite size and lattice distortions during the milling process, which provide information on the increase in inner energy of the powders resulting from mechanical activation. In addition, the powder characteristics were determined by the surface area and the particle size, which indicate the rise in surface energy.

#### Experimental procedure

Four different commercially available  $\text{Al}_2\text{O}_3$  powders of high purity were studied (Table 1). The three powders A, B and C are fused corundum powders. These three powders had an approximately equal average particle size between 3  $\mu\text{m}$  and 4  $\mu\text{m}$ . The values for the surface area, crystallite size and lattice distortions of the powders in their raw state are shown in Table 1. A commercial calcined powder with a relatively high surface area was

TABLE 1. Original characteristics of the  $\text{Al}_2\text{O}_3$  powders studied.

	Surface area m <sup>2</sup> /g	Crystallite size μm	Lattice Distortions %
Fused corundum			
Powder Al	3.75	0.14	0.04
Powder A2*	1.1	0.15	0
Powder B	0.95	0.15	0
Powder C	1.1	0.15	0.075
Calcined			
Powder D	10	0.058	0

\* Term for powder Al that has been burned for 1 h at 1200°C.

included in the study (powder D). According to the company's data, the calcination temperature for this powder was 900°C. Only the  $\alpha$ -modification could be detected by means of X-ray. In order to study the effect of milling on powders of the same average particle size and particle size distribution but with differing structural properties and varying content of flaws, powder Al was also burned for 1 h at 1200°C and then milled under the same conditions.

The milling studies were carried out in a planet mill with the addition of alcohol (mill tank 600 ml; filled volume approx. 1/3; three  $\text{Al}_2\text{O}_3$  milling balls, 30 mm Ø; rotation speed 1000/min). After various milling periods small amounts of powder were removed each time for X-ray and morphological examination. The effect of the milling process was followed by means of the crystallite size and lattice distortion structural properties which were determined by X-ray and by means of the surface area, determined by the BET method (determination of nitrogen adsorption at low temperatures). In addition the distribution of the particles was determined by means of an electron scanning microscope.

## Results and discussion

As is already known from numerous studies, mechanical activation rises with increased milling time. In the powders studied, mechanical activation is indicated mainly by the increase in surface area (Figure 2). In the five powders studied the surface area increases steadily with increased milling time. The largest increase is observed in powders A1, A2 and B with milling periods up to 60 h; beyond 90 h only a slight increase occurs. In contrast to this, the surface area of powder C rises constantly up to 150 h of milling time. The end results achieved differ considerably; in the fused corundum powders they are between 4.8 and 8.4  $\text{m}^2/\text{g}$ . The area of the burned powder A2 remains below the values of the unburned powder A1 during the entire period of milling. Powder B shows the least effect from milling. There is only a relatively slight increase in the surface area of the calcined powder, which is already very high to begin with.

It is known that during milling a reduction in the size of the agglomerate and the particles occur. Figure 3 shows the characteristic change in particle size distribution for the fused corundum powders studied; this figure shows diagrammatically the particle size distribution for powder C as determined by means of the electron scanning microscope, in its original state and after 10 h and 50 h of milling.

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Figures 4 and 5 show the changes in lattice distortions and crystallite size as functions of the length of milling time. In all the fused corundum powders mechanical activation is indicated by an increase in lattice distortions and a decrease in crystallite size. The considerable differences in the individual powders lie in the temporary change in structural properties and in the final values obtained for these two characteristics. The behavior of the powders during milling can be summarized in the following points:

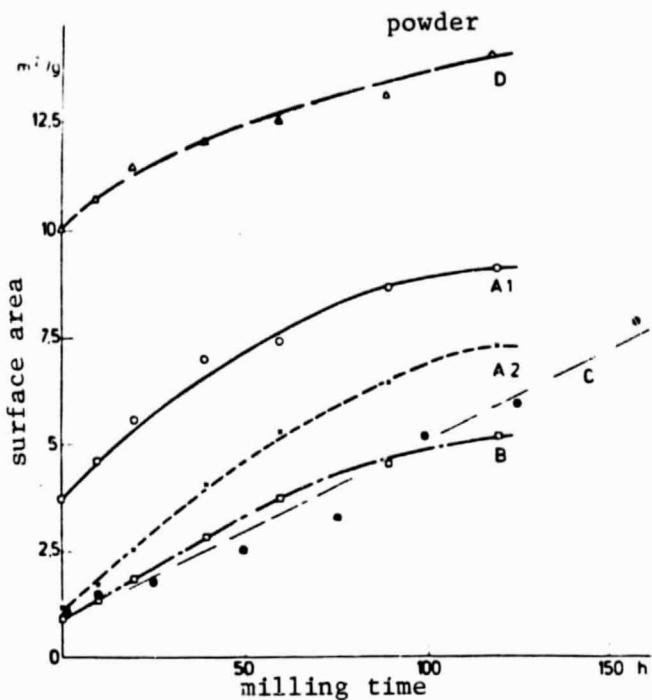


Figure 2. Changes in the surface area of different  $\text{Al}_2\text{O}_3$  powders during milling.

a) The curves of powders Al, B and C follow a similar course. After 40 h of milling a great increase in lattice distortions was observed simultaneously with a slight decrease in crystallite size. Longer milling produces a continuous decrease in crystallite size with only a slight increase in lattice distortions. Powder C behaves similarly to Powder Al.

b) The final values obtained for the individual powders were between 0.05% and 0.16% for lattice distortions and between 0.06  $\mu\text{m}$  and 0.09  $\mu\text{m}$  for the crystallite size. The milling behavior of powder B is striking, since it had a considerably lower number of lattice distortions but its crystallite size was very low, 0.06  $\mu\text{m}$  after more than 100 h of milling. The crystallites of this powder became smaller by a factor of about 2.5 during milling.

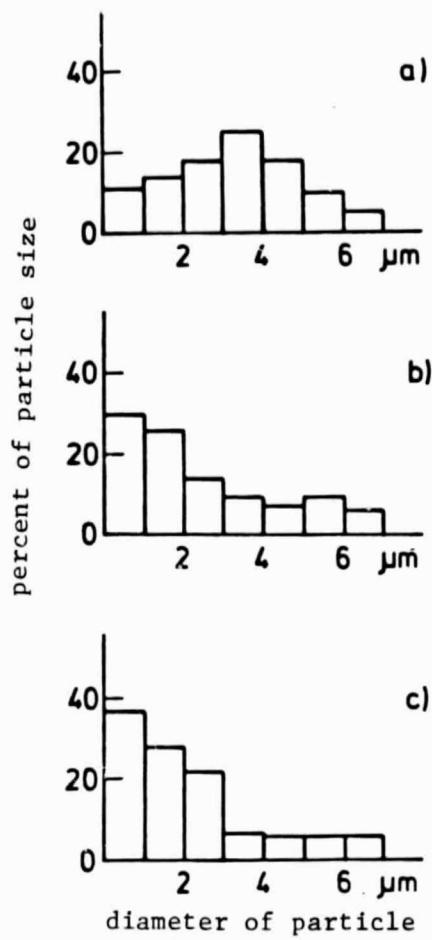


Figure 3. Frequency distribution of particle diameters during different milling periods. a) original unmilled powder; b) 10 h milling time; c) 50 h milling time.

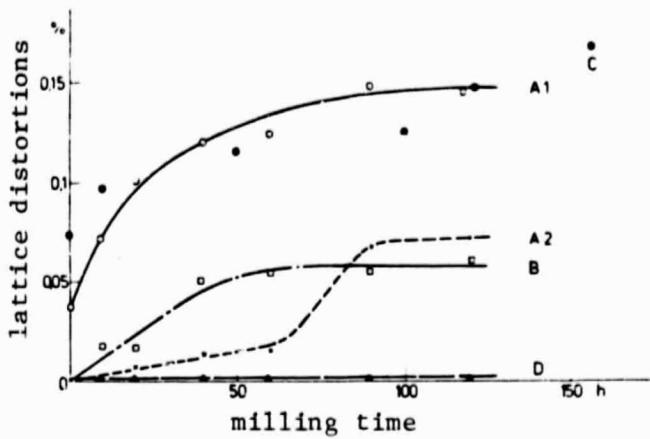


Figure 4. Changes in lattice distortions of different  $\text{Al}_2\text{O}_3$  powders during milling.

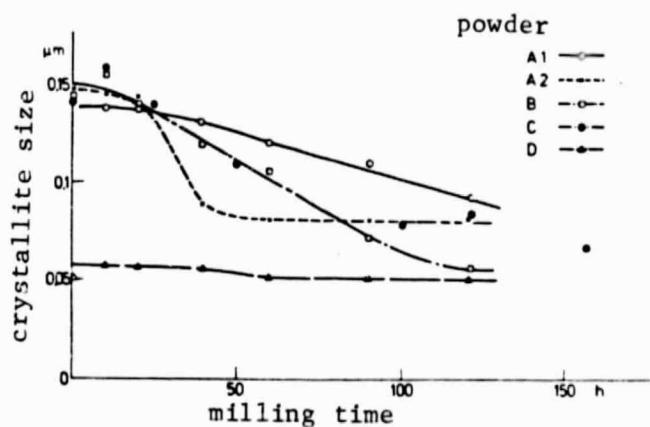


Figure 5. Changes in crystallite size of different  $\text{Al}_2\text{O}_3$  powders during milling.

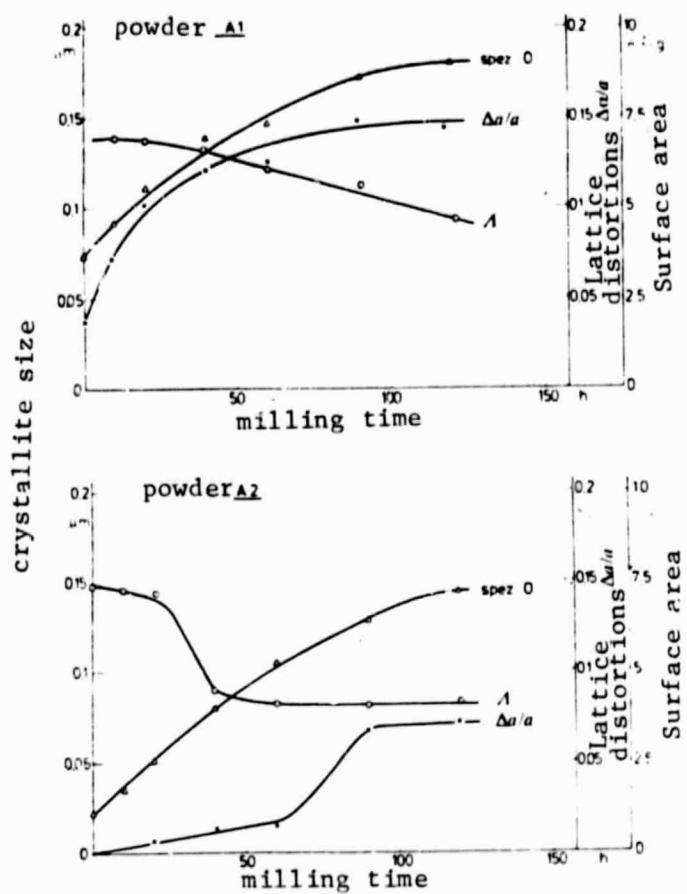


Figure 6. Changes in powder characteristics during milling of powder Al and of the burned powder A2 (powder Al heated for 1 h at 1200 °C).  
 a) Powder Al; b) powder A2.

c) The contrast in the properties of the unburned powder Al and the burned powder A2 shown in Figures 6a and 6b demonstrates clearly how different the effects of milling can be in  $\text{Al}_2\text{O}_3$  powders with the same particle size distribution. In the case of the unburned powder Al a considerable lattice strain is produced in the first 40 h and the crystallite size changes only slightly during this period, while in the case of the burned powder A2 the first 40 h of milling produces only a decrease in crystallite size. Longer milling up to 120 h produces a greater decrease in crystallite size in the unburned powder without the lattice strain increasing significantly. On the other hand, for the burned powder, milling up to 120 h produces an increase in lattice distortions although the crystallite size is almost exactly the same. Comparison of the increase in surface area with the structural changes shows that the differing pattern of structural changes in powders Al and A2 cannot be gauged by the surface area.

d) In contrast to the four fused corundum powders the calcined powder D, which has a low crystallite size of 0.058  $\mu\text{m}$  in the raw state, shows considerably different behavior during milling (see Figures 4 and 5). No lattice distortions occur in this powder during the entire milling period, and only a slight decrease in crystallite size is observed. From this it can be concluded that in this powder the increase in surface area is primarily the result of morphological changes, probably a decrease in agglomerate and particle size [15]. In addition, changes in the form and surface quality of the particles during milling may affect the surface area.

Mechanical activation during milling therefore produces an increase in surface area, a shift in particle size distribution to lower values, and, above all, an increase in the disordered condition of the lattice, which can be measured quantitatively by changes in lattice distortions and crystallite size. The milling experiments with  $\text{Al}_2\text{O}_3$  powders have shown that the chronological sequence and the degree of mechanical activation vary in the different powders. The calcined

powder showed almost no lattice structure changes during the entire period of milling. In the case of the fused corundum powders, mechanical activation can occur differently even in powders with approximately the same particle size in the raw state. The causes of this may be differences in the condition of the order in the lattice (see differences in the form and surface quality of the particles in the raw state. The surface area is not an indication of the differing changes in structural properties during milling. The final values obtained for lattice distortions differ by a factor of about 3; for crystallite size they differ by 50%. Since the changes in crystallite size and lattice distortions are a result of the presence of lattice flaws in the crystal lattice and of fracturing of the crystallites, measurement of the structural changes during milling provides quantitative information on the increase in energy content of the powders. Using simplified assumptions, the changes in crystallite size and lattice distortions in relation to the length of milling time allow certain conclusions to be drawn about the number and arrangement of the lattice flaws [12]. The changes in structure and surface area in relation to the length of milling time show clearly that, for the powders studied and the milling conditions in effect, milling times longer than 90 h do not produce any significant increase in activity. Greater mechanical activation is produced by introducing greater mechanical energy using other methods.

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